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(54) Title: POLYMER COMPOSITIONS (57) Abstract Thermoset polymer compositions of improved impact resistance comprise a metathesis polymerization product of 5-(3-cyclohexen-1-yl)-2-norbornene and from 2 to 10 % by weight of a block copolymer of vinylaromatic hydrocarbon compound and a conjugated alkadiene or a selectively hydrogenated derivative thereof.		

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POLYMER COMPOSITIONS

This invention relates to improved, impact resistant compositions comprising a thermoset olefin metathesis polymer derived from an adduct of 4-vinylcyclohexene and cyclopentadiene.

5 The production of polymers by the ring-opening or metathesis polymerization of cyclic and polycyclic olefins is well known. Numerous patent and literature references relate to the ring-opening polymerization of dicyclopentadiene in the presence of olefin metathesis catalyst systems.

10 The ring-opening polymerization of dicyclopentadiene produces a solid, hard, infusible polymer product of established utility. However, the polymerization and the resulting product suffer from a number of disadvantages. Unless the polymerization is relatively
15 quantitative, there will be unreacted monomer in the polymer product and a molded article produced therefrom will have an undesirable odor of dicyclopentadiene.

 Some of these disadvantages are improved by producing olefin metathesis polymer product from adducts of
20 4-vinylcyclo-hexene and cyclopentadiene (provided as dicyclopentadiene). The 4-vinylcyclohexene and cyclopentadiene react under Diels-Alder conditions to produce a mixture of adducts of the monomeric reactants as well as cyclopentadiene oligomers. The ring-opening polymerization
25 of the adduct/oligomer mixture results in a hard polymeric product free from a dicyclopentadiene odor (see US-A-5,095,082).

 A polymeric product having properties even more desirable for certain applications can be produced by the
30 ring-opening polymerization of 1:1 molar adducts of 4-vinylcyclohexene and cyclopentadiene, which adducts are isolated from the above-described mixture of vinylcyclohexene and cyclopentadiene adducts and cyclopentadiene oligomers

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(see WO 93/02121). The 1:1 adduct mixture, principally isomers of 5-(3-cyclohexen-1-yl)-2-norbornene, is recovered relatively free from other adducts and oligomers by conventional methods. The olefin metathesis polymerization of 5-(3-cyclohexen-1-yl)-2-norbornene results in a product of more desirable and more controllable mechanical properties, depending in part on whether crosslinking agents and, optionally, additional dicyclopentadiene, are also present in the polymerization mixture. Although these polymers have better elongation properties than olefin metathesis polymers of dicyclopentadiene, the polymers are still somewhat brittle and are not entirely suitable for applications wherein the polymers are likely to encounter impact by hard objects.

It is known to modify the impact properties of polydicyclopentadiene by the inclusion therein of elastomeric materials (see for example US-A-4,696,985). The resulting impact properties are better, but the polymers remain unsuitable for specific applications.

Japanese Patent Application 63-92640 describes the incorporation of other polymers in an olefin metathesis polymer of 5-(3-cyclohexen-1-yl)-2-norbornene as well as the addition of a variety of elastomeric materials to improve impact resistance including polybutadiene, polyisoprene, butyl rubbers, EPDM rubbers and block copolymers including styrene-butadiene-styrene and styrene-isoprene-styrene. No distinction is made among the listed elastomers and no supporting data are provided. Actual incorporation of such elastomers and evaluation of the resulting products has shown that not all the elastomers are not useful in improving impact resistance and the proportion of rubber added is also material. Incorporation of some elastomers serves to degrade the Gardner Impact strength. Moreover, incorporation of certain other elastomers improves one type of impact

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resistance, e.g. Gardner Impact, but not other types of impact resistance, e.g. Notched Izod Impact. It would be of advantage to provide compositions containing olefin metathesis polymers of 5-(3-cyclohexen-1-yl)-2-norbornene having broadly improved impact resistance as well as a method of improving the impact resistance of those polymers.

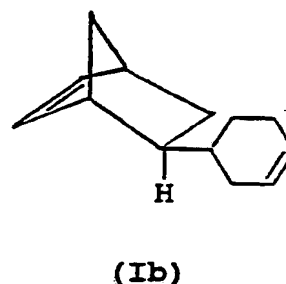
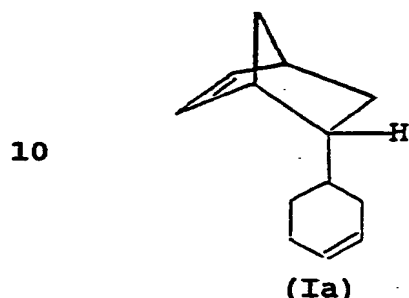
The present invention provides a thermoset polymer composition comprising a metathesis polymerization product of 5-(3-cyclohexen-1-yl)-2-norbornene and from 2 to 10% by weight, based on total composition, of an impact modifier selected from an elastomeric block copolymer of a vinylaromatic hydrocarbon compound and isoprene and a selectively hydrogenated derivative of an elastomeric block copolymer of a vinylaromatic hydrocarbon compound and a conjugated alkadiene.

The composition of the invention preferably comprises a major portion of the olefin metathesis polymerization product of a 1:1 adduct of 4-vinylcyclohexene and cyclopentadiene. A mixture of adducts is produced by heating 4-vinylcyclohexene and cyclopentadiene (provided as dicyclopentadiene) at elevated temperatures and thereby obtaining a mixture containing 1:1 adducts of 4-vinylcyclohexene and cyclopentadiene, 1:2 adducts and 1:3 adducts, as well as cyclopentadiene oligomers including cyclopentadiene trimers, tetramers and pentamers. The adduct mixture is prepared at elevated temperatures, typically from 180°C to 260°C, in an inert reaction environment. Traces of reactive materials such as oxygen should be excluded and the inclusion within the reaction mixture of free radical scavengers is also useful.

The resulting adduct/oligomer mixture can be separated by conventional methods such as chromatographic separation or fractional distillation, preferably under

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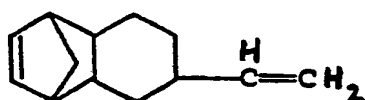
reduced pressure. The portion of the mixture particularly useful in providing a metathesis polymerization product for use in the compositions of the invention is a 1:1 adduct, principally 5-(3-cyclohexen-1-yl)-2-norbornene. This compound exists in isomeric forms represented by the formulas



15 The isomer of the formula Ia is termed an "endo" isomer and the isomer of formula Ib is termed an "exo" isomer as reflects the steric relationship of the cyclohexene substituent to the non-planar 6-membered ring of the norbornene moiety. Also produced by the process of adduct

20 formation is another isomeric form of 1:1 adduct represented by the formula

25



(II)

In the separation of the desired 5-(3-cyclohexen-1-yl)-2-norbornene isomers from the mixture of vinylcyclohexene and cyclopentadiene adducts and cyclopentadiene oligomers, an

30 initial preliminary separation is conveniently made with the use of a simple distillation column or a wiped film evaporator. A second and more effective separation is achieved through the use of a multi-tray distillation column.

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Careful separation typically provides 1:1 adduct mixtures having as high as 90% by weight and preferably as high as 95% by weight of a mixture of isomers Ia and Ib, although adduct mixtures having at least 80% by weight of 5-(3-cyclohexen-1-yl)-2-norbornene isomers are useful as precursors of the metathesis polymerization product component of the compositions of the invention. The remainder of the separated and recovered adduct mixture is typically the isomer of formula II with less than 5% and preferably less than 1% of unreacted 4-vinylcyclohexene and dicyclopentadiene, higher adducts and cyclopentadiene oligomers being present.

To obtain the compositions of the invention, the mixture of 5-(3-cyclohexen-1-yl)-2-norbornene isomers can then be subjected to olefin metathesis polymerization in the presence of an olefin metathesis catalyst system and the block copolymeric elastomer which is to be incorporated into the composition.

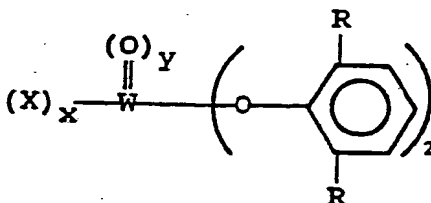
A variety of olefin metathesis catalyst systems are suitable, including those described in US-A-3,933,788; US-A-4,861,848, US-A-4,810,762 and EP-A-374997.

A preferred olefin metathesis catalyst system comprises a hexavalent tungsten halide, with from 0 to 1 oxygen substituent and alkylphenoxy substituents, which is employed in conjunction with an alkylaluminum compound or a triorganotin hydride, optionally additionally employed with a boron halide promoter. A preferred class of such tungsten halides is represented by the following formula as an average of several tungsten halides present.

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(III)

In the above formula III, each R independently is alkyl of up to 10 carbon atoms and is preferably branched alkyl of up to 6 carbon atoms such as isopropyl, sec-butyl or t-butyl. A particularly preferred R group is isopropyl. The term "X" is halo, e.g., bromo or chloro, but is preferably chloro. The term "x" is 2 or 4 and y is 0 or 1 with the sum of x + 2y being 4. The preferred tungsten compounds are therefore substituted tungsten halides if y is zero or oxychlorides if y is 1. Particularly preferred as the tungsten-containing catalyst system component are bis(2,6-diisopropylphenoxy)tungsten oxychloride and bis(2,6-diisopropylphenoxy)tungsten chloride.

When an alkylaluminum compound is used in conjunction with the tungsten halide, it is preferably an alkylaluminum chloride wherein any alkyl group is alkyl of from 2 to 8 carbon atoms inclusive. Ethylaluminum dichloride and diethylaluminum chloride are particularly preferred. Preferred for use in conjunction with the tungsten halide, however, is a triorganotin hydride, particularly a trialkyltin hydride wherein each alkyl independently is straight-chain lower alkyl of from 3 to 8 carbon atoms inclusive. Tri-n-butyltin hydride is particularly preferred.

In suitable olefin metathesis catalyst systems, molar ratios of alkylaluminum compound or triorganotin hydride to tungsten halide of the above formula III from about 2:1 to about 6:1 are satisfactory.

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It is useful on occasion to provide to the olefin metathesis catalyst system a boron halide promoter. Suitable promoters include boron trihalides, boron trihalide complexes and tetrahaloborates. A boron trifluoride etherate complex, e.g., boron trifluoride diethyletherate or boron trifluoride dibutyletherate, is preferred. The use of the boron halide promoter is optional and amounts of promoter up to 10 moles of promoter per mole of tungsten halide are satisfactory. When promoter is employed, amounts of promoter from about 0.01 mole to about 2 moles of boron halide promoter per mole of tungsten halide are preferred. Whether promoter is present or not, quantities of catalyst system sufficient to provide from about 0.001 mole percent to about 5 mole percent of tungsten halide based on total monomer mixture to be polymerized are satisfactory.

The compositions of the invention are suitably produced by polymerizing the 5-(3-cyclohexen-1-yl)-2-norbornene in the presence of the olefin metathesis catalyst system and the elastomeric component of the composition. While compositions incorporating a variety of elastomeric materials, both synthetic and natural, such as polybutadiene, polyisoprene, random copolymers of ethylene and propylene, terpolymers of ethylene, propylene and a diene monomer, or polymers of styrene, butadiene and acrylonitrile can be prepared, to obtain the benefits of the invention, however, the elastomeric material is selected from certain members of the class of elastomeric materials known as block copolymers of vinylaromatic hydrocarbon and alkadiene, as well as the selectively hydrogenated derivatives thereof. The block copolymers useful in the compositions of the invention, or as precursors for the selectively hydrogenated derivatives, are certain thermoplastic elastomers characterized by at least one block of at least predominantly polymerized vinylaromatic

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hydrocarbon compound (conventionally termed an A block) and at least one block of at least predominantly polymerized conjugated alkadiene (conventionally termed a B block).

The vinylaromatic hydrocarbon useful as the monomer of A blocks has a vinyl group, i.e., a $C=CH_2$ group, attached directly to an aromatic ring and has up to 12 carbon atoms inclusive. Preferred vinylaromatic hydrocarbons are styrene and styrene homologs such as those of the formula



15 wherein each R' independently is hydrogen or alkyl of up to 4 carbon atoms inclusive. Illustrative of such vinylaromatic hydrocarbons are styrene, p-methylstyrene, p-ethylstyrene, m-propylstyrene, α -methylstyrene, α -ethylstyrene and α ,4-dimethylstyrene. Styrene and α -methylstyrene are a preferred class of vinylaromatic hydrocarbons but particularly preferred is styrene.

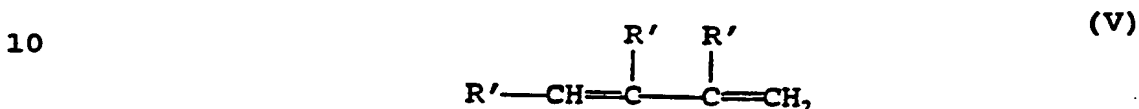
Each A block of the block copolymer independently is at least predominantly the polymerized vinylaromatic hydrocarbon and is preferably homopolymeric. Alternatively, however, one or more A blocks is a block wherein some of the monomer of block B is copolymerized with the predominant vinylaromatic monomer of block A. Such blocks are termed "tapered" and have at least 85% by mole and preferably at least 93% by mole of the vinylaromatic hydrocarbon with any remainder being the conjugated alkadiene of block B. The A blocks containing a mixture of vinylaromatic hydrocarbons are also useful but are less preferred. With regard to such block copolymers broadly, the average molecular weight of an A block is typically from about 1000 to about 125,000 but A

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blocks of molecular weight from about 5000 to about 60,000 are more often encountered.

Each B block of the block copolymer independently is a block of at least predominantly polymerized alkadiene.

- 5 The alkadienes useful as the predominant monomer for a B block are conjugated alkadienes of up to 8 carbon atoms such as those alkadienes of the formula



wherein R' has the previously stated significance.

- 15 Illustrative of such alkadienes are 1,3-butadiene (butadiene), 2-methyl-1,3-butadiene (isoprene), 2,3-dimethylbutadiene, 1,3-pentadiene (piperylene), 1,3-octadiene and 2-methyl-1,3-hexadiene. Preferred conjugated alkadienes are butadiene and isoprene. Each B block is at least
- 20 predominantly polymerized alkadiene with the B block being at least 85% by mole and preferably at least 93% by mole of polymerized alkadiene with any remainder being the vinylaromatic of block A in the case of tapered B blocks. Homopolymeric B blocks are preferred although the tapered
- 25 blocks and blocks of mixed alkadienes are also satisfactory. Within a polymerized alkadiene block two modes of polymerization are possible and are generally observed. In what is termed 1,4 polymerization, each carbon atom of the four carbon nucleus of the alkadiene is incorporated into the
- 30 polymeric chain which then includes two carbon atoms joined by an ethylenic linkage. In 1,2 polymerization, the polymerization includes only one carbon-carbon double bond of the conjugated alkadiene. The carbon atoms of that double bond will then be incorporated into the polymeric chain which

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will then contain a pendant olefinic group. Control of these two modes of polymerization is within the skill of the art. Preferred block copolymers are those wherein from about 5% to about 99% of the units of each B block are the result of 1,2 polymerization. Particularly preferred are those block copolymers wherein from about 8% to about 50% of the units in each B block result from 1,2 polymerization. The average molecular weight of a B block is suitably from about 10,000 to about 450,000, preferably from about 10,000 to about 150,000.

Within the block copolymer, the A block content is not more than about 55% by weight, based on total block copolymer. Preferably, the A block is from about 10% by weight to about 40% by weight on the same basis. The total average molecular weight of the block copolymer will be on the order of from about 11,000 to about 450,000, but preferably from about 35,000 to about 300,000. These average molecular weights are determined by conventional techniques such as gel permeation chromatography or by low angle light scattering or combinations thereof.

The structure of the block copolymer will depend upon the method of polymerization employed to produce the polymer. In one modification, the block copolymer is termed linear and is illustratively produced by sequential polymerization of the blocks. By way of example, in the production of a three-block or triblock copolymer, the vinylaromatic hydrocarbon of the A block is polymerized with the aid of an initiator, preferably an alkyl lithium compound. The conjugated alkadiene of the B block is then introduced and subsequently the additional vinylaromatic hydrocarbon for a second A block. Such a three-block copolymer is characterized as ABA. A two-block or diblock copolymer is produced by polymerizing an A block with the aid of an

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alkyllithium initiator and subsequently introducing the conjugated alkadiene required for a B block. Such a polymer is characterized as AB. Substantially complete polymerization of one monomer before addition of the other monomer results in the production of homopolymeric blocks. If, however, prior to the complete polymerization of any one block the monomer of the next block is introduced, tapered blocks will result. Similar sequential polymerization techniques are employed to produce block copolymers characterized as ABABA, ABAB, ABABABA or polymers of an even higher number of blocks. Production of block copolymers, particularly those of relatively high molecular weight, is also accomplished by the use of a coupling agent to couple or connect growing polymer chains. Use of a difunctional coupling agent such as a dihaloalkane will result in the production of linear polymers but use of a coupling agent having a functionality of three or more, e.g., polyvinyl aromatic hydrocarbons, silicon tetrahalides or alkyl esters of dicarboxylic acids, will result in the formation of block copolymers variously termed "star", "radial" or "branched".

These block copolymers are well known in the art and the characterization and preparation of such polymers are illustrated by U.S. 3,251,905, U.S. 3,390,207, U.S. 3,598,887, U.S. 4,219,627, U.S. 4,408,357, U.S. 4,497,748 and U.S. 4,426,495.

The block copolymer types most commonly encountered are linear sequential polymers of the types polystyrene-polybutadiene (SB), polystyrene-polyisoprene (SI), polystyrene-polybutadiene-polystyrene (SBS) and polystyrene-polyisoprene-polystyrene (SIS). This same type of nomenclature is conventionally used for other types of block copolymers, e.g., SBBS or (SB)₂ for coupled linear polymers and (SB)_n for radial polymers of n arms of SB segments

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arranged around a central core. These block copolymers are conventional and a number are commercial, being marketed by Shell Chemical Company as KRATON® Thermoplastic Rubber.

To obtain the olefin metathesis products of broadly improved impact resistance, however, the nature of the block copolymer is of substantial importance. The copolymers which provide the best impact resistance are those wherein the A block is relatively small compared to the total copolymer molecule. Preferred block copolymers for the compositions of the invention are those wherein each A block has a molecular weight of less than about 20,000, more preferably less than about 12,000 and the B block is polyisoprene. Preferably, the polyisoprene block will result from at least 90% and more preferably at least 95% of 1,4 polymerization.

Also useful in the compositions of the invention are selectively hydrogenated derivatives of the block copolymers as above described. To prepare these derivatives, the block copolymers are selectively hydrogenated by a process sufficient to hydrogenate from about 80% to about 99% of the aliphatic unsaturation of each B block, but no more than 25% and preferably no more than 5% of the aromatic unsaturation of each A block. Such hydrogenation is accomplished by conventional methods illustrated by the disclosures of U.S. 3,113,986 and U.S. 4,226,952. The selectively hydrogenated block copolymer is often identified by the structure of the block copolymer precursor and the "apparent" structure of the aliphatic block. Thus, selective hydrogenation of a SBS polymer will result in a polymer having a hydrogenated mid-block which is "apparently" polyethylene in the case of a mid-block produced by 1,4 polymerization and ethylene/butylene copolymer in the case of a polymer mid-block produced with random proportions of 1,2 and 1,4 polymerization. These selectively hydrogenated block

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copolymers are indicated by SES and SEBS respectively. A corresponding selectively hydrogenated diblock copolymer would be termed SE or SEB. The selective hydrogenation of a SIS block copolymer of a high degree of 1,4 polymerization in the mid-block is termed an SEPS polymer because of the similarity of the hydrogenated mid-block to an ethylene/propylene copolymer. The most commonly encountered selectively hydrogenated block copolymers are linear of the SES and SEBS type wherein units of the mid-block are from about 20% to about 90% and preferably from about 30% to about 50% of the mid-block type resulting from 1,2 polymerization with the remainder being substantially of the type resulting from 1,4 polymerization. An illustrative selectively hydrogenated "radial" type copolymer is correspondingly illustrated by $(SE)_n$ or $(SEB)_n$ where n represents the number of SB arms present prior to the selective hydrogenation. The selectively hydrogenated block copolymers and the characterization thereof are well known in the art with a number being commercial. For example, certain of the selectively hydrogenated block copolymers are marketed by Shell Chemical Company as KRATON G[®] Thermoplastic Rubber.

When the selectively hydrogenated block copolymers are employed in the compositions of the invention, it is preferred to employ such copolymers with relatively small A blocks as compared to the total molecule. Selectively hydrogenated block copolymers having A blocks of molecular weight below about 30,000 are preferred and selectively hydrogenated block copolymers having A blocks of molecular weight below about 20,000 are particularly preferred. The preferred selectively hydrogenated block copolymers contain a percentage of "B" blocks derived from polymerization of butadiene by 1,2 and 1,4 polymerization, i.e., blocks with EB configuration, of at least 45% wt and less than about 85% wt.

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The compositions of the invention are produced when specified quantities of the block copolymer or selectively hydrogenated derivative thereof is added to the polymerization mixture containing 5-(3-cyclohexen-1-yl)-2-norbornene, which may also contain olefin metathesis polymerization crosslinkers and, optionally, dicyclopentadiene. The ring-opening or metathesis polymerization under conventional polymerization conditions of this mixture produces the polymerization product incorporating the elastomeric material. The proportion of the elastomeric material in the total composition is suitably from about 2% by weight to about 10% by weight based on total composition. Proportions of elastomeric material from about 4% by weight to about 8% by weight are preferred.

The compositions of the invention are toughened thermoset polymers useful in conventional applications for such polymers but particularly useful in applications where a polymeric product is likely to be subject to impact by other objects. Specific applications for the compositions of the invention include parts and housings for automotive applications.

The invention is further illustrated by the following Comparative Examples (not of the invention) of the Illustrative Embodiments which should not be regarded as limiting.

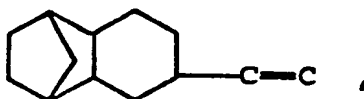
Illustrative Embodiment I

Dicyclopentadiene and 4-vinylcyclohexene in equimolar mixture were heated in an autoclave at 240°C for 4 to 4.5 hours. The reaction product was diluted with cyclohexane and passed through a packed bed of alumina in order to remove the t-butylcatechol inhibitor introduced with the reactants. The resulting mixture was distilled in a wiped film evaporator at 400 pa (3 mm Hg) pressure and 90°C

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to afford a light fraction containing unreacted vinylcyclohexene and dicyclopentadiene. A 50g sample of this distillate was vacuum distilled using a 10-tray Oldershaw column to give four fractions. The fourth fraction, 65g, was shown by gas chromatographic analysis to consist of 0.15% dicyclopentadiene, 88.3% endo-5-(3-cyclohexen-1-yl)-2-norbornene, 6.1% exo-5-(3-cyclohexen-1-yl)-2-norbornene, two additional components, present in the amounts of 1.9% and 2.4%, are believed to be isomeric adducts of the formula

10



several additional components totalling about 0.4%, about 0.4% tricyclopentadiene and about 0.4% mole unidentified components. Analysis of the fraction by nuclear magnetic resonance indicated about 87 mole% of the above endo adduct, about 9% of the above exo adduct and about 5% of isomeric adducts of the above formula II.

Illustrative Embodiment II

A number of moldings of compositions of the invention were produced and evaluated. The production of moldings was by one of two general procedures. The solutions of elastomer in monomer were prepared by combining under nitrogen the appropriate proportions of dried monomer and dried elastomer and mixing to dissolve the elastomer. In some cases an antioxidant such as 2,6-di-t-butyl-4-methylphenol was also dissolved in the monomer in quantities from 0.2% wt to 0.5% wt.

General Procedure - 10 cm x 10 cm (4" x 4") Plaque

30 Moldings

In a Vacuum Atmospheres dry box under nitrogen, a 30 ml dry silanized serum bottle was charged with a predetermined amount of bis(2,6-diisopropylphenoxy)tungsten

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oxydichloride (7% by weight, in monomer), boron trifluoride dibutyl etherate (1% by weight, in monomer) and a dry solution of the elastomer in additional monomer to provide a total of 25 gm of monomer solution. The resulting mixture
5 was mixed vigorously. A second serum bottle was charged with tributyltin hydride (a 4:1 molar ratio of tin to tungsten) and 25g of elastomer in monomer.

The two solutions were allowed to sit undisturbed for at least 5 minutes to allow bubbles to rise to the top of
10 the bottle. The solutions were then poured into a 50 ml dual barrel plastic cartridge with end caps and rear pistons were inserted. The cartridge was then placed in a screw cap jar along with a 15 cm (6") disposable static mixer. The jar was then closed and transferred from the dry box to a Manostat
15 plexiglass glove box under nitrogen.

The cartridge was removed from the jar and loaded into a ConProTec dispensing gun, the end cap of the cartridge was replaced by the static mixer and the polymerization mixture was injected through the mixing tube into a
20 preheated, nitrogen-purged mold in the glove box. The temperature in the mold was observed and the time to an exotherm was noted. The sample was left in the mold 5 minutes after the exotherm and the heater was then disconnected and the mold opened. In some cases the molded
25 plaque was then removed from the mold but in other cases the plaque was allowed to remain in the mold until the temperature reached 80°C. A typical molding temperature was 100°C to 140°C (before exotherm), the molar ratio of monomer to catalyst was generally 2000:1 to 6000:1, typically 4000:1,
30 and the molar ratio boron trifluoride (if used) to catalyst was 0.05-0.15, typically 0.075:1.

The mold consisted of silicone rubber flexible heaters sandwiched by 15 cm x 15 cm (6" x 6") stainless steel

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plates on the interior of the mold and insulating board on the exterior. Thermocouples are inserted between the plates and the flexible heaters. A flexible polytetrafluoroethylene beading gasket, 0.292 cm (0.115") diameter is used to control the thickness of the plaque at about 0.279 cm (0.110"). The plates and gaskets are held together with large clamps and the mold uses two screw-in injection ports for injection and overflow, with the injection port at the bottom.

General Procedure - Large Plaque Moldings

10 In a Vacuum Atmospheres dry box a 250 ml bottle, which had been rinsed with toluene and acetone and dried overnight in an oven, was charged with a predetermined amount of the tungsten catalyst solution (from about 2000 to about 5000 moles of monomer per mole of tungsten) described above, 15 the boron trifluoride (about 0.05 mole to about 0.15 mole per mole of tungsten) in solution (if used) and a crosslinking monomer (if used). Additional monomer or rubber solution in monomer was charged to provide 70g of the monomer mixture. A second bottle was charged with 70g of the monomer or rubber 20 solution and tributyltin hydride (typical molar ratio of tin to tungsten of 4:1). The contents of each bottle were thoroughly mixed and the bottles were placed in the antechamber of the dry box and subjected to several vacuum cycles to degas the solutions.

25 Each solution was poured into a 75 ml plastic cartridge with end cap and a rear piston was inserted. The end caps were removed and after any excess nitrogen was removed the caps were replaced and the cartridges were joined in a double barrelled system. The sealed cartridges were 30 then removed from the dry box.

In a fume hood, a mold consisting of Watlow silicone rubber flexible heaters sandwiched by 18 x 28 cm

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(7" x 11") aluminum plates and having external insulating board was constructed. The back plates had thermocouples in the surface of the plate and the front plate had a thermocouple inserted through a hole in the side of the plate to near the center. The interior surfaces were treated with a mold release agent and a gasket made from 0.3 cm (1/8") Teflon beading was placed between the plates approximately 1.9 cm (0.75") from the outside edge. The plates had injection and overflow ports and the mold was held together with large clamps. Prior to molding, the mold was purged with nitrogen and heated to the desired molding temperature, typically 100°C to 120°C.

The end caps of the cartridges were removed and replaced by a static mixer tube. The cartridge pair was loaded into a "gun" and the two monomer solutions were forced from the cartridges, through the static mixer and into the preheated mold. The injection time, exotherm temperature and time to exotherm were noted. The sample was left in the mold for 5 minutes when the heater was disconnected and the plaque removed. In some cases, the plaque was allowed to remain in the mold until the mold had cooled to about 80°C, about 10-15 minutes.

25 Comparative Example I - Illustrative Embodiments III-IV

General Procedure

A number of compositions of the invention were produced by the above procedures and evaluated for impact resistance. Tests to determine two conventional types of impact resistance were employed. To determine the value for Gardner impact by a process similar to ASTM D-3029, a plaque of about 0.3 cm (1/8-inch) thickness of the candidate composition is produced by conventional molding methods and a

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cylindrical rod of known weight is dropped from predetermined heights onto a flat side of the plaque. This test measures the impact sensitivity of the composition and failure is noted when the sample cracks upon impact. A second type of impact test, the notched Izod test, is determined by a test similar to ASTM D-256 and employs a molded specimen about 0.3 cm (1/8-inch) thick with a notch on one edge. The sample is struck by a pendulum from a predetermined height on the notched side. The test measures the energy required to break the sample at the notch.

Although both of these tests are conventional, they measure different impact failures of the sample being tested. It is common that a composition will provide satisfactory results from one test but not in the other. It is less common that a composition will provide satisfactory results in both tests.

Comparative Example I

Compositions were prepared by polymerizing a 5-(3-cyclohexen-1-yl)-2-norbornene mixture in the presence various block copolymers of styrene and butadiene. The types of block copolymer or elastomer were as follows:

- Elastomer A: Coupled, linear tri-block copolymer of the (SB)₂ type
- Elastomer B: Radial block copolymer of the (SB)₃ type having three polybutadiene/polystyrene arms.
- Elastomer C: Similar to Elastomer B with 3 or 4 arms per molecule.

The compositions were evaluated for Gardner and Notched Izod impact resistance and the results are shown in Table I. The molecular weight of the styrene blocks therein and the other Illustrative Embodiments are weight average molecular weights.

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TABLE I

	<u>Elastomer (%wt)</u>	<u>Styrene Block (Mw x 10⁻³)</u>	<u>Gardner Impact J (in-lb)</u>	<u>Izod Impact J/cm(ft-lb/in)</u>
5	None (0)	-	39.6 (350)	0.27 (0.5)
	A (5)	10.2	45.2 (400)	0.75 (1.4)
	(6)	10.2	33.9 (300)	0.21 (0.4)
	(7)	10.2	33.9 (300)	0.91 (1.7)
10	(8)	10.2	3.4 (30)	0.16 (0.3)
	(4)	16.1	-	0.27 (0.5)
	(6)	16.1	10.2 (90)	-
	B (6)	11.5	33.9 (300)	0.27 (0.5)
	(8)	11.5	5.6 (50)	0.27 (0.5)
15	C (6)	12.0	13.6 (120)	-
	(6)	21.0	<6.8 (<60)	0.37 y(0.7)

Many of the results from the Gardner Impact testing are considered satisfactory. The results from the Izod Impact testing are unsatisfactory.

Illustrative Embodiment III

A series of compositions containing a block copolymer of styrene and isoprene were produced and evaluated according to the procedure of Comparative Example I. The elastomer employed, Elastomer D, was linear, coupled tri-block copolymer of the (S-I)₂ type. The results of the evaluation are given in Table II.

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TABLE II

5	<u>Elastomer (%wt)</u>	<u>Styrene Block (Mw x 10⁻³)</u>	<u>Gardner Impact J (in-lb)</u>	<u>Izod Impact J/cm(ft-lb/in)</u>
	D (6)	10.6	33.9 (300)	-
	(7)	10.6	27.1 (240)	5.77 (10.8)
	(6)	10.8	30.5 (270)	-
10	(7)	10.8	-	4.4 (8.2)
	(6)	10.9	31.6 (280)	-
	(7)	10.9	-	4.7 (8.8)
	(6)	15.5	3.16 (280)	-

- 15 The results obtained from both Gardner Impact testing and Izod Impact testing are considered satisfactory.

Illustrative Embodiment IV

- A series of compositions containing selectively hydrogenated block copolymers of styrene and butadiene were produced and evaluated according to the procedure of Illustrative Embodiment III. The types of elastomeric components employed were as follows.

- 25 Elastomer E: Linear, coupled copolymer of the type (S-EB)₂
- Elastomer F: Linear, sequential copolymer of the type SEBS

The results of the evaluation are shown in Table III.

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TABLE III

5	<u>Elastomer (%wt)</u>	<u>Styrene Block (Mw x 10⁻³)</u>	<u>Gardner Impact J (in-lb)</u>	<u>Izod Impact</u>	
				<u>J/cm (ft-lb/in)</u>	
10	E (4)	7.2	45.2 (400)	0.5	(0.9)
	(5)	7.2	40.7 (360*)	0.7	(1.3*)
	(6)	7.2	39.6 (350)	0.8	(1.5)
	(7)	7.2	35.0 (310*)	6.8	(12.7*)
	(8)	7.2	36.2 (320)	5.9	(11.1)
15	F (4)	7.2	45.2 (400)	0.4	(0.7)
	(5)	7.2	38.4 (340)	7.85	(14.7)
	(6)	7.2	33.9 (300)	1.2	(2.2)
	(7)	7.2	24.9 (220)	0.32	(0.6)
	(8)	7.2	14.7 (130)	0.37	(0.7)
20	(5)	9.4	32.8 (290)	1.6	(3.0)
	(6)	9.4	13.6 (120)	0.43	(0.8)
	(7)	9.4	10.2 (90)	0.37	(0.7)
	(8)	9.4	20.3 (180)	0.43	(0.8)
25	(4)	10.1	-	10.6	(13.3)
	(5)	10.1	39.6 (350)	1.2	(2.2)
	(6)	10.1	28.2 (250)	0.32	(0.6)
	(7)	10.1	21.5 (190)	0.37	(0.7)
	(8)	10.1	16.9 (150)	0.5	(0.9)
30	(4)	29.0	31.6 (280)	0.27	(0.5)
	(6)	29.0	33.9 (300)	2.1	(4.0)

* Average of tests on more than one molding

In all cases where the Izod Impact is satisfactory, the Gardner Impact is also satisfactory.

40 Comparative Example II

A metathesis polymerization product was prepared from the mixture of adducts and cyclopentadiene oligomers prepared by heating 4-vinylcyclohexene and dicyclopentadiene according to the procedure of Illustrative Embodiment I.

45 Without separation, the mixture was polymerized by a

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procedure similar to that of Illustrative Embodiment II in the presence of 7% by weight of Elastomer E. The value obtained for the Gardner Impact was 15.8 J (140 in-lb) and the value for Notched Izod Impact was 0.43 J/cm (0.8 ft-
5 lb/in).

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CLAIMS

1. A thermoset polymer composition comprising a metathesis polymerization product of 5-(3-cyclohexen-1-yl)-2-norbornene and from 2 to 10% by weight, based on total composition, of an impact modifier selected from an elastomeric block copolymer of a vinylaromatic hydrocarbon compound and isoprene and a selectively hydrogenated derivative of an elastomeric block copolymer of a vinylaromatic hydrocarbon compound and a conjugated alkadiene.
2. A composition according to claim 1 wherein the impact modifier is a block copolymer of styrene and isoprene.
3. A composition according to claim 2 wherein the molecular weight of each polystyrene block is less than 20,000.
4. A composition to claim 2 or 3 wherein the block copolymer is a linear block copolymer.
5. A composition according to claim 2 wherein the block copolymer is an at least triblock copolymer.
6. A composition according to claim 5 wherein the block copolymer is an ABA or an (AB)₂ block copolymer of styrene and isoprene.
7. A composition according to claim 2, 3, 5 or 6 wherein at least 90% of the units in each polyisoprene block result from 1,4 polymerization.
8. A composition according to claim 1 wherein the impact modifier is a selectively hydrogenated derivative of an

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elastomeric block copolymer of a vinylaromatic hydrocarbon compound and a conjugated alkadiene resulting from the hydrogenation of at least 80% of the aliphatic unsaturation but no more than 25% of the aromatic unsaturation of the elastomeric block copolymer.

9. A composition according to claim 8 wherein the modifier is a selectively hydrogenated derivative of styrene and butadiene or isoprene.

10. A composition according to claim 9 wherein the molecular weight of each styrene block is less than 30,000.

11. A composition according to claim 8 wherein the modifier is a selectively hydrogenated derivative of a linear block copolymer.

12. A composition according to claim 11 wherein the selectively hydrogenated block copolymer is an at least triblock copolymer.

13. A composition according to claim 8, 9, 10, 11 or 12 wherein the hydrogenated alkadiene comprises from at least 45% to less than 85% of the total weight of the copolymer.

14. A composition according to claim 8, 9, 10, 11 or 12 wherein the selectively hydrogenated block copolymer is a polymer of the SEBS or (SEB)₂ type.

15. A composition according to claim 1, 2, 3, 5, 6, 8, 9, 10, 11 or 12 wherein the impact modifier is present in an amount from 4 to 8% by weight based on total composition.

16. A process for producing a thermoset polymer product as claimed in claim 1, 2, 3, 5, 6, 8, 9, 10, 11 or 12 which

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comprises the olefin metathesis polymerization of 5-(3-cyclohexen-1-yl)-2-norbornene in the presence of an olefin metathesis polymerization catalyst system and from 2 to 10% by weight of said impact modifier.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/04520

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08G61/08; C08L65/00; C08L53/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08G ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,5 095 082 (SHELL OIL COMPANY) 10 March 1992 cited in the application see claim 1 ---	1
A	PATENT ABSTRACTS OF JAPAN (C-525)5 September 1988 & JP,A,63 092 640 (TEIJIN) 23 April 1988 cited in the application see abstract ---	1
A	EP,A,0 387 662 (NIPPON ZEON) 19 September 1990 see claims 1,4; examples ---	1-7, 16
A	EP,A,0 468 595 (SHELL) 29 January 1992 comp. example c d see table 1 ---	1, 16
-/--		
<p>¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 07 JULY 1993	Date of Mailing of this International Search Report 28.07.93	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer KLIER E.K.	

Form PCT/ISA/210 (second sheet) (January 1983)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>DATABASE WPIL Week 9116, 19 June 1991 Derwent Publications Ltd., London, GB; AN 91-113469 & JP,A,3 054 220 (JAPAN SYNTHETIC RUBBER) 8 March 1991 see abstract</p> <p>-----</p>	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9304520
SA 74683

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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07/07/93

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